

DE 33 12 328 A1

(Offenlegungsschrift) German Patent No. DE 3312328 A1

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Translated from German by the Ralph McElroy Company, Custom  
Division, P.O. Box 4828, Austin, TX 78765 USA

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## GERMAN PATENT OFFICE

(Offenlegungsschrift)

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AGENT FOR FINAL RINSING IN MACHINE WASHING OF LAUNDRY	
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The present invention pertains to an agent for the machine treatment of laundry at the conclusion of the actual machine wash cycle, by which the formation of incrustations is prevented and incrustations that are present can be removed. Besides softeners, the agent contains organic acids, especially di-, tri-, and/or polycarboxylic acids.

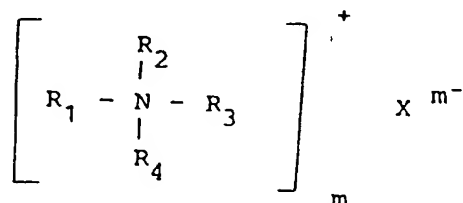
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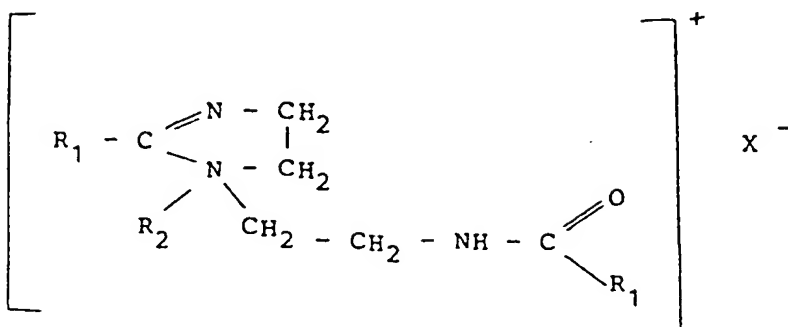
#### Patent claims

1. Agent for final rinsing in the machine washing of laundry containing a quaternary textile softener of the general formula

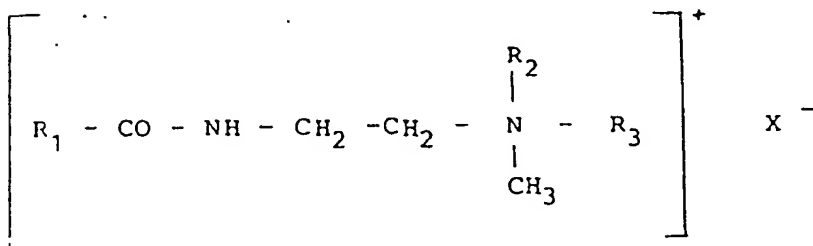


wherein  $R_1$  and  $R_2$  are hydrocarbon groups with 16-22 carbon atoms,  $R_3$  and  $R_4$  are hydrocarbon groups with 1 to approximately 4 carbon atoms,  $X$  is an anion, and  $m$  is a whole number of 1-3,

or imidazolinium compounds of the general formula

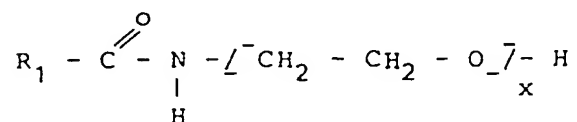


wherein  $\text{R}_1$  is a straight-chained or branched hydrocarbon group with 8-25 carbon atoms,  $\text{R}_2$  is hydrogen or a hydrocarbon group with 1-4 carbon atoms, and X is an anion or textile softening compounds such as alkylated amidoamines of the general formula



wherein  $\text{R}_1$  is a straight-chained or branched hydrocarbon group with 8-25 carbon atoms,  $\text{R}_2$  [and]  $\text{R}_3$  are hydrocarbon groups with 1-4 carbon atoms, and X is an anion

or fatty acid derivatives such as glycerin monostearate,  
 mixtures of glycerin mono- and distearates,  
 or fatty acid amidoethoxylates of the general formula:



wherein  $R_1$  is a straight-chained hydrocarbon group with 12 to 24 carbon atoms,

wherein the above-indicated substances can be used alone or in combination, characterized by consisting of organic acids, especially di-, or tri-, or polycarboxylic acids, with alkaline earth and heavy metal ion complexing properties.

2. Agent for final rinsing according to Claim 1, characterized by a carboxylic acids content of 0.5-50 wt.%.

3. Agent according to Claims 1-2, characterized by the fact that it contains di-, tri-, or polycarboxylic acids or mixtures thereof in combination with monomeric [sic; monofunctional] carboxylic acids with a carbon number of 1 to 3.

4. Agent according to Claims 1-3, characterized by the fact that it contains citric acid as the organic carboxylic acid.

5. Agent according to Claims 1-4, characterized by the fact that it contains di-, tri-, or polycarboxylic acids or mixtures thereof in combination with phosphonic acids.

6. Agent according to Claims 1-5, characterized by the fact that the di-, tri-, or polycarboxylic acids or mixtures thereof are used in combination with aminopolycarboxylic acids.

7. Agent according to Claims 1-6, characterized by the fact that it contains 0.3-10% of a nonionic surfactant of the classes  
alkyl polyglycol ethers  
alkylaryl polyglycol ethers  
fatty acid polyglycol ethers  
fatty acid amide polyglycol ethers [or]  
alkylamine polyglycol ethers.

8. Agent according to Claims 1-7, characterized by the fact that it additionally contains dyes, perfumes, preservatives, and optical brighteners.

9. Use of agents according to Claims 1-8 in washing machines in the last rinse.

10. Process for the softening of laundry, characterized by the fact that the wash is treated with systems of cationically active substances in amounts of 0.5-50% and multifunctional carboxylic acids in amounts of 0.5-50%.

11. Process according to Claim 9, characterized by the fact that the wash is treated in the washing machine with 0.5-6 g/L of the system containing cationically active substances and multifunctional carboxylic acids.



Agent for final rinsing in machine washing of laundry

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The invention pertains to an agent and a process for the treatment of laundry in washing machines, which leaves the textiles in a softened condition and increases the utility value of the laundry and the machine.

The treatment of [previously] worn and soiled articles of clothing in washing machines is done with the goal of retaining the utility value properties of the wash, which besides cleanliness (the targeted soil removal), includes a series of additional points such as absorbability, air permeability, wear resistance, [and] softness.

The functions of phosphates in detergents are many and are closely related to retaining the utility value of the wash, but also of the washing machine. Besides the most important task, [namely] complexing of the hardness formers in the water used and thus preventing deposits on the wash and the washing machine parts, the phosphates have a dispersing and emulsifying capacity, they synergetically increase the surfactant effect, [and] they form a complex with heavy metals. Condensed phosphates, especially pentasodium triphosphate, are the most important components of alkaline washing and cleaning agents (CH-PS [Swiss patent] No. 179,075).

Until the end of the 70s, detergents contained phosphates in adequate amounts so that, even in hard water, incrustations were hardly (on the order of less than 1%) encountered when adequate amounts of detergent were used.

Due to legally mandated decreases in the phosphate content of detergents or in the wash water, a decrease in the eutrophication called forth by the phosphates in surface waters was strived for.

However, the utility properties of the wash are negatively affected by the decrease in the amount of phosphates in detergents or decreased amounts of phosphates in washing machine water, and the materials used as replacements, such as zeolites, do not attain the originally positive results.

Commercial detergents with a decreased phosphate content, e.g., corresponding to the Phosphathöchstmengenverordnung [Ordinance on Maximum Amounts of Phosphates] in Germany, produce textile incrustations of 4-6% (after 15 washes) even in moderately hard water; at a high water hardness, the values of textile incrustation (after 25 washes) easily increases to 10%.

Due to increased textile incrustation, which is also associated with increased deposition on machine parts, the utility value of the wash is negatively affected to the extent that the absorbability and air permeability are decreased, and therefore all the clothin physiological properties are negatively affected. Due to increased textile incrustation, the absorption of soil in the incrustation also negatively affects the washing results. The useful life of the clothing is also negatively affected since the wear resistance of textiles with high [amounts of] incrustations decreases. Formation of a coating is also noted to an increased extent on machine parts, primarily on heating elements.\* Heat

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\* [German machines typically are supplied with cold water which is heated in the machine.]

buildup and the inclusion of corrosively acting ions are the consequences that decrease the useful life of the heating elements.

A series of studies intended to prevent or inhibit incrustation have been presented. Thus, e.g., it has been suggested that one work in a washing system that has acid and alkaline partial steps within the washing process, wherein in the alkaline partial step, the precipitation of ions that create water hardness as calcium salts is accepted, i.e., incrustations are acceptable. Only the cumulative effect that usually occurs is prevented by this. See e.g., Chem. Abstr. 92 (1980) 24.

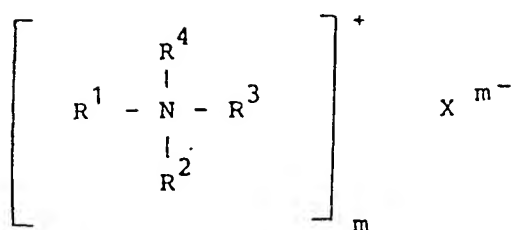
In addition, products are known which are capable of imparting a soft feel to the treated wash, the so-called softeners. However, these have the disadvantage that they do not affect incrustations in the wash or in the machine.

It has now been shown, surprisingly, that it is possible to retain the utility properties of the wash and washing machines if, in the last treatment bath of the washing cycle, the claimed agents are used, with these containing a textile softener and acids [and] organic carboxylic acids, especially di-, tri-, and polycarboxylic acids.

The agents of the invention for retaining the utility value of the wash and washing machine contain:

- a textile softener of the quaternary ammonium compound type or [an] imidazolinium compound or other softening compounds [and]
- acids, especially di-, tri-, or polycarboxylic acids.

The quaternary ammonium compounds have the general formula



wherein  $R_1$  and  $R_2$  are hydrocarbon groups with 16-22 carbon atoms, [and]  $R_3$  and  $R_4$  are hydrocarbon groups with 1-4 carbon atoms. In the indicated formula,  $X$  can be any salt-binding anion, e.g., a halide, hydroxide, sulfate, carbonate, or phosphate. The charge of the anion is indicated as  $m^-$ , wherein  $m$  is 1-3.

The number of cationic ammonium groups is identical to the charge,  $m$ , of the anion so that electrical neutrality prevails. Quaternary ammonium compounds in which  $m = 1$  are commercially available, and for this reason are preferred for use in the agent of the invention.

Listed below are examples of quaternary ammonium compounds that are suitable for use in the agent and in the process of the present invention:

ditallowdimethylammonium chloride

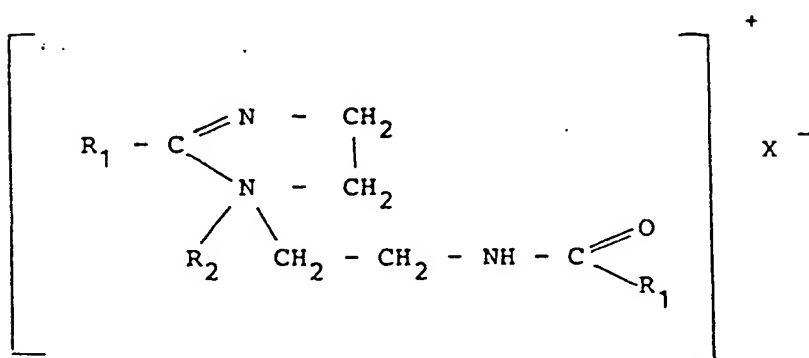
distearyldimethylammonium methyl sulfate

dicetyldimethylammonium chloride

didocosyldimethylammonium chloride

dodecyldimethylammonium chloride  
 ditallowdimethylammonium bromide  
 ditallowdibutylammonium fluoride  
 cetyldecylmethylethylammonium chloride

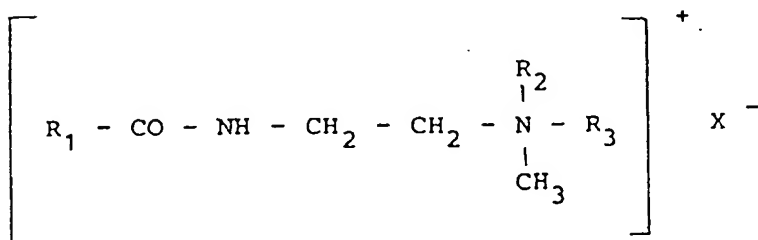
Likewise, imidazolinium compounds of the general formula are suitable:



wherein  $\text{R}_1$  is a straight-chained or branched hydrocarbon group with 8-25 carbon atoms,  $\text{R}_2$  is a hydrogen atom or a hydrocarbon group with 1-4 carbon atoms, and X is an anion.

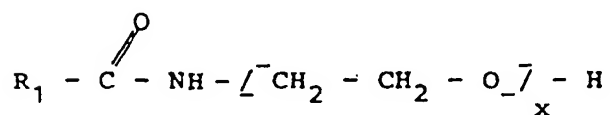
e.g., 1-fatty alkylamidoethyl-2-fatty alkyl-3-methylimidazolinium  
 methyosulfate [methyl sulfate]

Likewise, textile softening compounds are suitable, such as alkylated amidoamines of the general formula:



wherein  $R_1$  is a straight-chained or branched hydrocarbon group with 8-25 carbon atoms,  $R_2$  [and]  $R_3$  are hydrocarbon groups with 1-4 carbon atoms, and  $X$  is an anion

or fatty acid derivatives such as glycerin monostearate, mixtures of glycerin mono- and distearates, or fatty acid amidoethoxylates of the general formula:



wherein  $R_1$  is a straight-chained hydrocarbon group with 12 to 24 carbon atoms.

The acids used in the agent of the invention are in particular di-, tri-, and polycarboxylic acids, which possibly are hydroxy-substituted or unsaturated and have a complexing

effect on alkaline earth and heavy metal ions. The acids can possibly be used in the form of mixtures. As examples, without attempts at completeness, the following can be named:

Dicarboxylic acids:

oxalic acid  
malonic acid  
succinic acid  
glutaric acid  
adipic acid  
pimellic acid  
mesoxalic acid

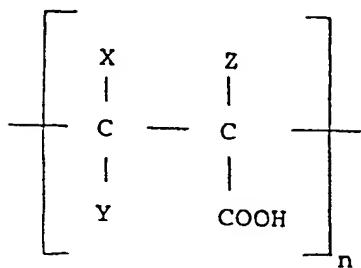
Unsaturated dicarboxylic acids:

maleic acid  
fumaric acid

Hydroxy-, di-, and tricarboxylic acids:

tatronic [sic; tartronic] acid  
malic acid  
tartaric acid  
citric acid  
aconitic acid

Polycarboxylic acids of the general formula:



wherein X, Y, and Z can be hydrogen, methyl, aryl, acryl, carboxyl, hydroxy, or carboxymethyl groups, [i.e.] polycarboxylic acids such as:

butanetetracarboxylic acid

cyclopentanetetracarboxylic acid

Citric acid has shown itself to be especially suitable.

Besides the complexing di-, tri-, or polycarboxylic acids, possibly monomeric [monofunctional] carboxylic acids, e.g., formic acid or acetic acid, can be used.

Besides the complexing di-, tri-, or polycarboxylic acids, possibly phosphonic acids can be used, e.g.:

ethane-1-hydroxy-1,1-diphosphonic acid

nitrilo-tris-methylenephosphonic acid

diethylenetriaminepentamethylenephosphonic acid, [and]

N,N-dimethyluridomethanediphosphonic acid.

Besides the complexing di-, tri-, or polycarboxylic acids, possibly aminocarboxylic acids can be used, e.g., trinitrilotriacetic acid, ethylenediaminetetraacetic acid, [and] diethylenetriaminepentaacetic acid.

Besides the textile softener and the complexing acids, the agent of the invention contains nonionic surfactants in small amounts, e.g., condensation products of compounds containing carboxylate, hydroxyl, amino, [or] amido groups with ethylene oxide.

Perfumes, dyes, optical brighteners, [and] preservatives can be incorporated as needed in amounts substantially less than 1%.

Via the use of carboxylic acids of the invention, it is



possible, surprisingly, to produce systems that contain complexing agents in adequate amounts in the presence of cationically active surfactants.

The composition of the agent and the process for retaining the utility value of the wash and the washing machine are described in more detail by the following examples.

Example 1:

1.5 kg of an acid mixture consisting of adipic acid at 28%, glutaric acid at 47%, [and] succinic acid at 25% are dissolved at 50°C in 7.65 kg of water in a 20-L stirred vessel. 0.1 kg of a C<sub>14</sub>-C<sub>15</sub> oxoalcohol with 7 mol of EO [ethylene oxide] (Dobanol 45 E-7) were added with stirring.

0.75 kg of 75% dialkyldimethylammonium chloride (the rest is water/isopropanol) (Präpagen WK) were added in the molten state with stirring.

The agent of the invention was used in a Bauknecht WA 1805 washing machine in the last treatment bath. 90 mL were used in each case.

The agent of the invention was used immediately after the wash at 90°C. The water hardness in all cases was 28°d [German degrees of hardness; 1°d = 10 mg/L CaO]; 10 washing cycles were done in each case.

[As] a comparison to the agent of the invention, a commercial softener with 7% dialkylmethylammonium chloride (Präpagen WK) was used.

As Table II shows, the incrustation of the wash is significantly decreased by the agent of the invention and the formation of deposits on the heating elements (washing machine parts) are also significantly decreased.

Examples 2-8 shown in Table I were produced by the appropriate addition of water, dissolution of acid, addition of nonionic surfactant, introduction of the textile softener where intended, cooling, [and] introduction of a perfume.

Table I

Examples (in wt% in each case)

Dialkyldimethylammonium chloride

(Präpagen WK)

(Präpagen WKL)

Imidazolinium compound

(Rewoquat W7500)

Fatty acid amidoethoxylate

(Lutensol FSA 12)

Glycerin monostearate

(Tegin M)

Fatty alcohol ethoxylates:

(Dobanol 45 7 E)

(Alfol 1214 6 EO)

Nonylphenoloethylate [sic]:

(Marlophen 87)

Acid mixture:

(adipic acid 28%)

(glutaric acid 47%)

(succinic acid 25%)

Citric acid

Cyclopentanetetracarboxylic acid

Perfume

2	3	4	5	6	7	8
	7	7				2,5
5,5						
2		2				
			3	3	3	2
			5	5	5	5
	0,5		1,0	1,0	1,0	1,0
1,5						
15						15
		15	21	21	15	
	15					
0,3	0,3	0,3	0,3	0,3	0,3	0,3

Table II

② Behandlung erfindungsgemäß nach Beispielen

	① Vergleich		1	3	2	4	5	6	7	8
	A	B								
Waschmittel ③										
TPP-haltig ④	+	+	+	+	+	+	+	+	+	+
TPP/Zeolith-haltig ⑤										
Gewebeart ⑥										
Baumwolle ⑦										
Baumwolle/Polyester ⑧	+	+	+	+	+	+	+	+	+	+
Gewebeasche (8) ⑨	4,6 1,3	4,4 1,2	2,9 0,5	1,9 0,4	3,3 0,65	2,1 0,3	0,5 0,2	0,1 0,4	2,0 0,4	3,1 0,6
Heizstab ⑩	⑪ belegt	⑪ belegt	⑫ schwach belegt	⑫ schwach belegt	⑫ schwach belegt	⑫ schwach belegt	⑫ frei	⑬ frei	⑫ schwach belegt	⑫ schwach belegt

Key: 1 Comparison  
2 Treatment according to the examples of the invention  
3 Detergent  
4 TPP containing  
5 TPP/zeolite containing  
6 Type of textile  
7 Cotton  
8 Cotton/polyester  
9 Textile ash (%)  
10 Heating element  
11 Coated  
12 Weakly coated  
13 Free